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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/EP98/08295 <b>(22) International Filing Date:</b> 17 December 1998 (17.12.98) <b>(30) Priority Data:</b> 10/011377 23 January 1998 (23.01.98) JP <b>(71) Applicant (for all designated States except US):</b> MERCK PATENT GMBH [DE/DE]; Frankfurter Strasse 250, D-64293 Darmstadt (DE). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> NAKANISHI, Kazuki [JP/JP]; 64-10 Shimogamo Tadekura-cho, Sakyo-ku, Kyoto 606-0806 (JP). SOGA, Naohiro [JP/JP]; 4-3-23 Shinohara Honmachi, Nada-ku, Kobe 657-0067 (JP). MINAKUCHI, Tokiyo [JP/JP]; MRC Corporation, 3-59, Ohnmiya Syakadani, Kita-ku, Kyoto 603-8478 (JP). <b>(74) Common Representative:</b> MERCK PATENT GMBH; Frankfurter Strasse 250, D-64293 Darmstadt (DE).		<b>(81) Designated States:</b> US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> PROCESS FOR PRODUCING INORGANIC POROUS MATERIAL IN A CAPILLARY  <b>(57) Abstract</b>  Inorganic porous materials contained in a confined space with at least one dimension of less than 1 mm, which are in liquid tight contact with the walls of said confined space are disclosed. Capillaries are preferred as confined space. Processes for making such inorganic materials contained in a confined space.		

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### Process for producing inorganic porous material in a capillary

The present invention is related to a process for producing inorganic porous materials in a capillary (or more generally in a confined space as defined below) and materials prepared by such process. These materials are favorably applied to producing capillary columns for electrochromatography, porous catalysts, or enzyme supports. Such inorganic porous columns can be favorably applied to liquid, gel-permeation and gas chromatography. These columns can be used unmodified or modified e.g. by covering their surface with molecules like hydrophobic hydrocarbon ligands (e.g. octadecyl ligands) or like hydrophilic ligands like 2,3-dihydroxypropyl derivatives. The ligands of such modified columns can be further modified using known procedures. Porous catalysts or enzyme supports can be prepared by adding enzymes, e.g. glucose isomerase, or catalytic metal elements, e.g. platinum and palladium.

The sol-gel method is one of liquid phase reaction paths to produce inorganic porous materials, especially silica gels. The sol-gel method denotes widespread processes in which polymerizable low molecular weight species are first generated, and through polymerization reactions, aggregated or polymerized materials are finally obtained. For example, the sol-gel method can be applied by hydrolyzing metal alkoxides, metal chlorides, metal salts or coordinated compounds which typically contain carboxyl or beta-diketone ligands. A process of this kind is disclosed in EP 0 363 697. In this process an organic polymer is used, which is compatible with the solution of the metal alkoxide or its polymer, and which undergoes phase separation during the hydrolysis-polymerization step. The materials produced by this process display connected open pores with a narrow range of the pore size distribution. Improvements to the process as disclosed in EP 0 363 697 are subject matter of WO 95/03 256 and WO 98/29 350. WO 95/03 256 disclose the use of special pore forming agents, whereas WO 98/29 350 disclose the use of precursors of such pore

forming agents. All three documents disclose procedures useful to produce monolithic porous bodies. Common to the procedures disclosed in these three documents is that the porous formed body produced is taken out of the cast used for forming it. Such a procedure is not amenable if the porous formed body has a small dimension in at least one direction, because such thin structures would easily be teared or break. On the other hand the procedures disclosed in these three documents do not yield porous bodies which are fit liquid tight to their cast, because the inorganic material shrinks considerably during processing.

The existing capillary columns for electrochromatography is produced by packing inorganic materials such as silica gel beads into a capillary by physical means. It is necessary for the column packing materials used in the electrochromatography to carry electrostatic charge on their surfaces. Accordingly, inorganic porous materials which retain stable negative charges in a neutral pH condition, especially silica gels, are widely used.

Particle-packed capillary columns for electrochromatography have been prepared by physically packing inorganic particulate materials into a capillary. In order to avoid the change in the packing state of the particles due to their motion in the capillary, the both ends of a capillary are fitted with the parts called "frit" with relatively low porosity.

Particle-packed capillary columns are disadvantageous in the points that: (a) the packing procedure is complicated and time-consuming. (b) the reproducibility of the packing state, and correspondingly that of an excellent analytical performance, is poor. (c) Since the homogeneous packing of an entire capillary becomes increasingly difficult as the column length increases, an improvement of the analytical performance by increasing the total column length is not practical.

In addition, particle-packed capillary columns equipped with the frits at both ends frequently causes bubbling at the space between the frit and packed-beds, thus requires additional pressurization to the normal chromatographic operation.

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In spite of the fact that the analytical performance of a capillary column is governed by its inner porous structure directly related to the packing state of the particles, there has been no established particle-packing method which produces the stable and reproducible packing state.

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Figure 1 shows the size distribution of mesopores measured for a sample gel prepared according to Example 1. Figure 2 shows the electrochromatogram of thiourea obtained using the capillary column described in Example 1.

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The problem of the present invention is to provide monolithic porous bodies with at least one small dimension, which are useful e.g. as sorbents in micro scale separations or as support media for catalysts or immobilized enzymes.

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This problem is solved by the present invention. The present inventors have found that: A capillary column which exhibits homogeneous and continuous double pore structure through the whole length of the capillary can be obtained by the processes of; 1) to form a three-dimensional continuous network consisting of an inorganic gel phase and a solvent phase both having average domain size of larger than 100 nm via a sol-gel process from a solution precursor containing a thermally decomposable component in a capillary with the inner diameter of less than 1 mm, 2) to modify the nanometer-range microstructures by heating the wet gel to decompose said thermally decomposable component, 3) to dry and heat-treat the gel to obtain completely inorganic porous material.

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A capillary with an inner diameter of less than 1 mm as mentioned above is the preferred modification of the invention, e.g. the specialized case of a confined space with a small dimension in at least one direction as defined in the problem to be solved by the invention. Accordingly unless explicitly stated, a capillary can be replaced by any other confined space with a small dimension in at least one direction. In this context a small dimension is defined as less than 1 mm, preferably between 10 and 200  $\mu\text{m}$ . Other examples of confined spaces with a small dimension in at least one direction are: three- or four-sided prisms or thin plates. Typically at least one dimension, e.g. the length of these structures, can be larger, separation capillaries might be one or several centimeters long, or even longer. Plates would be thin (less than 1 mm), but could be broader than 1 mm, e.g. one or several centimeters, up to about 20 cm broad. In all cases the porous formed body is enclosed by such a confined space, whereby a liquid tight contact area between porous formed body and confined space is provided.

The present invention has been developed based on the above knowledge. The invention provides capillary columns with a well-defined and highly reproducible internal pore structure through the whole length of the capillary and with an excellent analytical performance; instead of those packed with particles by conventional physical methods which has been defective in homogeneity, reproducibility and analytical performance.

One means of the present invention to attain said object is characterized by previously dissolving a thermally decomposable compound in a reaction solution, forming, from said reaction solution through its sol-gel conversion in a capillary, a gel that comprises a solvent-rich phase containing three-dimensionally networked open pores having a mean pore diameter of not smaller than 100 nanometers and an inorganic substance-rich skeleton phase containing particles each having fine pores on its surface, then

heating the wet gel to thermolyze said thermally decomposable compound existing in the reaction system, and thereafter drying and heating the gel.

5 In one preferred embodiment of said means, silica  $\text{SiO}_2$  is used as the inorganic substance while an amide compound, such as urea, capable of making the reaction system basic through its thermolysis is used as the thermally decomposable, low-molecular compound.

10 Another means of the present invention also to attain said object is characterized by dissolving a water-soluble polymer and a thermally decomposable compound in an aqueous acidic solution, adding thereto a metal compound having hydrolyzable functional groups to thereby hydrolyze said compound, solidifying the resulting product in a capillary, then heating the wet gel to thereby thermolyze the thermally decomposable low  
15 molecular compound existing in said gel, and thereafter drying and further heating the gel.

The substance to be added to the starting metal alkoxide is one having the function of inducing both sol-gel conversion and phase separation at the  
20 same time. Using this, the reaction system is separated into a solvent-rich phase and a skeleton phase, which being gelled. As the substance of that type, preferred is a polymer soluble in solvents, such as polyethylene oxide, polyvinyl pyrrolidone, polyethylene imine and polyallylamine.

25 The metal alkoxide is preferably a silicon alkoxide, which may include, for example, tetramethoxysilane, tetraethoxysilane, methyltrimethoxysilane, ethyltrimethoxysilane and vinyl trimethoxysilane. However, these are not limitative. The metallic elements corresponds to those contained in the desired oxide phase can be Si, Ti, Zr or Al. Both alkoxides containing  
30 single or multiple kinds of metals can be used. The oligomers of the alkoxides, usually up to decamers, can be used as far as they dissolve or disperse homogeneously in the solvent alcohol.

The acidity of the aqueous solution used to hydrolyze the metal alkoxide is preferably stronger than 0.001 mol/L of mineral acid such as hydrochloric acid or nitric acid.

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The capillary, made of fused silica for example, should have an inner diameter of less than 1 mm, preferably between 10 and 200  $\mu\text{m}$ . Similarly instead of capillaries containers which form inside them thin prisms of similar dimensions or thin plates with a thickness of less than 1 mm can be used.

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For the liquid tight junction between rod and capillary, the capillary wall should have high affinity with the gelling silicate components components in the solidifying solution. For example; (1) materials with surface hydroxyl groups which can undergo condensation with silanols, (2) relatively polar organic polymer surfaces which can physically adsorb silicate oligomers, (3) any other material which is surface-treated with hydrophilic layers; all of these can realize the liquid tight junction.

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Materials with very high water-repellency, such as PTFE resin or surfaces modified with fluorine-containing reagents, are not appropriate to make the liquid tight junction by the chemical means described above. In this special case, the use of thermoshrinking PTFE resin makes it possible to physically liquid tight clad after the formation of the gel body inside the capillary, by heating the resin capillary up to around 300  $^{\circ}\text{C}$  so as to obtain satisfactory cladding. The dimension of the confined space, diameter of a capillary or gap between the parallel walls etc., should be in

30



the size range smaller than 1 mm and preferably smaller than 100 microns.

5 The hydrolysis and polycondensation reaction is conducted under the conditions of; temperature between 40 and 80 °C, reaction time between 0.5 and 5 hours. The hydrolysis and polycondensation follows the steps of; 1) initially transparent solution becomes gradually opaque due to the phase separation into a gel phase and a pore-forming phase, 2) the whole solution turns into gel. During the whole reaction steps the water-soluble  
10 polymer is molecularly dissolved in the solution and no effective precipitation occurs.

One embodiment of the present invention for producing a porous inorganic material, in which the pore structure of the porous inorganic material can  
15 be most effectively controlled, is sol-gel conversion which comprises starting from a metal alkoxide and adding a suitable substance to said starting compound to thereby give a structure of a solvent-rich phase that produces macro-pores.

20 In the method of the present invention, where a water-soluble polymer and a thermally decomposable compound are dissolved in an aqueous acidic solution and a metal compound having a hydrolyzable functional group is added thereto to thereby hydrolyze said metal compound, formed is a gel comprising a solvent-rich phase and a skeleton phase as separated from  
25 each other in the capillary. After the product (gel) is solidified and then ripened for a suitable period of time, the wet gel is heated whereby the thermally decomposable compound that has been previously dissolved in the reaction system is thermally decomposed, resulting in the increase in the pH of the solvent that is kept in direct contact with the inner walls of  
30 particles constituting the skeleton phase. As a result, the solvent corrodes said inner wall to thereby change the inner surface of said inner wall into a

roughened one, whereby the pore-size of said particles is gradually enlarged.

5 For the gel consisting essentially of silica, the degree of said change in an acidic or neutral region will be very small, but with the increase in the thermolysis to enlarge the basic degree of the aqueous solution, the part constituting each pore is dissolved and re-precipitated to give a more flat part, thereby inducing more active reaction to enlarge the mean pore size.

10 If the gel has only fine and three-dimensionally restrained pores without having any macro-pores, even its part capable of being dissolved under equilibrated conditions could not produce a dissolved substance capable of being diffused into the external solution, so that the original fine pore structure will remain in the gel to have a relatively large proportion. As  
15 opposed to this, if the gel has a solvent rich-phase capable of giving macro-pores, it contains a large amount of only two-dimensionally restrained fine pores, so that the exchange of substances between said solvent-rich phase and the external aqueous solution may be effected well frequently in the gel, resulting in the removal of fine pores with the growth  
20 of macro-pores in the gel while preventing the entire pore size distribution of the resulting gel from being broadened.

25 In the thermolyzing step, it is effective to put the gel in a closed condition in order to make the vapor pressure of the thermally decomposed product saturated and to rapidly make the solvent have a steady pH-value.

Specific examples of the thermally decomposable compound employable herein may include urea, and organic amides such as formamide, N-methylformamide, N,N,-dimethylformamide, acetamide, N-methylacetamide, and N,N-dimethylacetamide. However, as will be mentioned in the Examples to follow hereinunder, the thermally decomposable compound is not limited to these, but may be any one capable of making the solvent basic after its thermolysis, since the pH value of the solvent after the thermolysis (final pH) is an important factor in the method of forming the mesopores. Similary, thermally-decomposable compounds which generate alternative substances which are capable of dissolving silica, e.g. hydrofluoric acid, can also be used. In addition, those capable of producing a compound having the property of dissolving silica, such as hydrofluoric acid, through thermolysis are also usable in the present invention. Such pore forming agents or precursors of pore forming agents are disclosed in WO 95/03 256 and in WO 98/29 350.

The amount of the thermally decomposable compound (precursor of pore forming agent) to be in the reaction system of the present invention may vary, depending on the type of said compound. For urea, for example, its amount may be from 0.1 to 2.0 g, preferably from 0.2 to 1.0 g, per 10 g of the reaction system. The heating temperature for the thermolysis of urea may fall between 60 °C and 200 °C, and, after the thermolysis, the final pH of the solvent is preferably from 9.0 to 11.0.

After the dissolving and re-precipitating reaction has reached its steady condition, the thermolyzing time for obtaining the corresponding pore structure may vary, depending on the size of the intended macro-pores and the volume of the reaction system being processed. Therefore, it is important to determine the shortest thermolyzing time, over which the pore structure of the gel is no more substantially changed under the processing conditions. For example, where urea is used as the thermally decomposable compound and the thermolyzing temperature falls between 60 °C and

200 °C, the thermolyzing temperature falls between 30 days (at 60 °C) to 100 hours (at 200 °C).

5 From the processed gel, the solvent is evaporated off, whereby the gel is dried to be a dry gel which is coherently attached to the inner wall of the capillary with the inner diameter of less than 1 mm. Since there is a probability that some starting compounds will still remain in the dry gel, the dry gel is thereafter heated at suitable temperatures to thereby further  
10 pyrolyze the remaining organic substances. As a result of the heat treatment, the intended porous inorganic material is finally obtained. Generally, the drying is conducted at the temperature between 40 and 100 °C for several to several tens hours, whereas the heat-treatment is performed in the temperature range between 300 and 700 °C.

15 The porous inorganic materials to be obtained according to the method of the present invention have three-dimensionally networked, open through-holes of not smaller than 100 nm in diameter, and fine pores of from 5 to 100 nm in diameter as formed on the inner walls of said through-holes. The porous inorganic materials of the present invention can be used in manu-  
20 facture of chromatography columns, adsorbent and filters, which, however, are not limitative.

Without further elaboration, it is believed that one skilled in the art can, using the preceding description, utilize the present invention to its fullest  
25 extent. The preferred specific embodiments and examples are, therefore, to be construed as merely illustrative, and not limitative of the disclosure in any way whatsoever.

The entire disclosures of all applications, patents, and publications cited above and below, and of corresponding Japanese Application number JP - hei 10-11377, filed January 23, 1998, are hereby incorporated by reference.

5

## EXAMPLES

### Example 1

10 Firstly, 0.90 g of poly(ethylene oxide) (product No. 85645-2, manufactured by Aldrich, Molecular weight: 10000) and 0.90 g of urea were dissolved in a 10 g of 0.01 mol/l aqueous solution of acetic acid. Then 4 ml of tetra-  
methoxysilane was mixed with this solution under stirring to promote  
hydrolysis reaction. After a few minutes stirring, the resultant transparent  
15 reaction solution was transferred to a capillary with the inner diameter of 0.1 mm (100  $\mu$ m) and sealed, which gelled in 30 min at a constant temperature oven kept at 40 °C.

20 The solidified sample was further aged at the same temperature for several hours, then heated up to 120 °C and kept at the temperature for 1 h under tightly sealed condition. The pH of the solution in contact with the gel sample was 10.7. The gel was subsequently dried for 3 days and was heated up to 400 °C with the heating rate of 100 °C/h. With these  
25 processes, a porous amorphous silica filled in a capillary with the inner diameter of 0.1 mm was obtained.

It was confirmed by the electron microscopic observation that in the porous silica material thus formed in the capillary, uniform macropores with a pore size of about 2.0micrometer were present in an interconnected manner. In  
30 addition, the nitrogen adsorption measurement evidenced the existence of mesopores with average diameter of 25 nm in the inner wall of the said gel sample. Figure 1 shows the pore size distribution of the mesopores.

In addition, when the porous materials were manufactured under the same conditions as described above except that the temperature of aging in tightly sealed condition was changed to 80 °C or 200 °C, the distributions  
5 of the macropores were not affected, but the median size of mesopores measured by the nitrogen adsorption varied to about 15 nm and 50 nm for 80 °C and 200 °C, respectively. From these results, it was shown that larger median size of mesopores can be obtained as the temperature of aging in tightly sealed condition increased.

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The capillary column thus prepared, with the effective length of 25cm, was set in an electrochromatography apparatus, and thiourea was analyzed at the temperature of 20 °C and with the applied electric voltage of 20 kV, adopting the mobile phase consisting of (acetonitrile: 50 mM of tris buffer  
15 solution) = 80:20 adjusted at pH=8.

The linear velocity of electro-osmotic current obtained under the conditions specified above was 1.19 mm/s, which was comparable to those observed in well-packed conventional particle-packed capillary columns.

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Figure 2 shows the elution peak of thiourea obtained under the conditions specified above. The number of theoretical plates calculated from the peak width was 48000 plates against 25 cm, which is comparable to the value of well-packed conventional particle-packed column; 200,000 plates/m.

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### Example 2

The capillary columns were manufactured under identical conditions to those described in Example 1 except that the amount of urea was 0.45 g to adjust the final value of the solution pH in contact with the gel sample to 9.

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The median mesopore sizes of the resultant gels were 15, 25 and 50 nm at 80, 120 and 200 °C, respectively. These results were in accordance with those obtained in the Example 1 within the range of experimental error, which implies that the median mesopore size hardly depend on the concentration of urea, but the widths of the mesopore size distribution became broader at all temperatures. These results show that with an increase in the concentration of urea in the starting solution, the mesopore distribution width became narrower and the specific mesopore volume became larger.

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With the capillary columns thus obtained, it was possible to perform similar electrochromatographic separation of thiourea as described in the Example 1.

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### EFFECT OF THE PRESENT INVENTION

As described so far, according to the present invention, it is possible to manufacture porous materials with controlled pore distribution in a capillary with the inner diameter of less than 1 mm. Presently invented inorganic porous column has outstanding features owing to its double-pore structure comprising interconnected macropores and tailored mesopores; the column requires no physical packing procedure for its production and can be suitably applied as a monolithic capillary column for electrochromatography, capillary electrophoresis, solid phase micro-extraction and gas chromatography.

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**Claims**

1. Process for producing inorganic porous materials contained in a confined space with at least one dimension of less than 1 mm, which  
5 comprises of the steps of,
- 1) provide a container as a confined space with at least one dimension of less than 1 mm;
  - 2) provide an acidic solution containing a water-soluble organic polymer and a thermally decomposable component together with a  
10 metalorganic compound containing hydrolyzable ligands;
  - 3) fill said solution into said container and form a three-dimensional co-continuous network consisting of an inorganic gel phase and a solvent phase both having average diameter of larger than 100 nm via a sol-gel process from a homogeneous solution precursor  
15 containing a thermally decomposable component;
  - 3) heat said container to modify the nanometer-range microstructures by heating the wet gel within the container to decompose said thermally decomposable component,
  - 4) to dry and heat-treat the gel contained in said container to obtain  
20 completely inorganic porous material.
2. Process for producing inorganic porous materials described in Claim 1 in which the inorganic phase is silica and the thermally decomposable component is urea.  
25
3. Process for producing inorganic porous materials described in Claim 1 in which the inorganic phase is silica and the thermally decomposable component is a compound which contains amide or alkylamide ligands.  
30



4. Process as described in one of the claims 1 - 3, wherein the confined space with at least one dimension of less than 1 mm is a capillary with an inner diameter of less than 1 mm.
5. Inorganic porous material contained in a confined space with at least one dimension of less than 1 mm, which is in liquid tight contact with the walls of said confined space.
6. Inorganic porous material of claim 5, wherein the confined space with at least one dimension of less than 1 mm is a capillary with an inner diameter of less than 1 mm.

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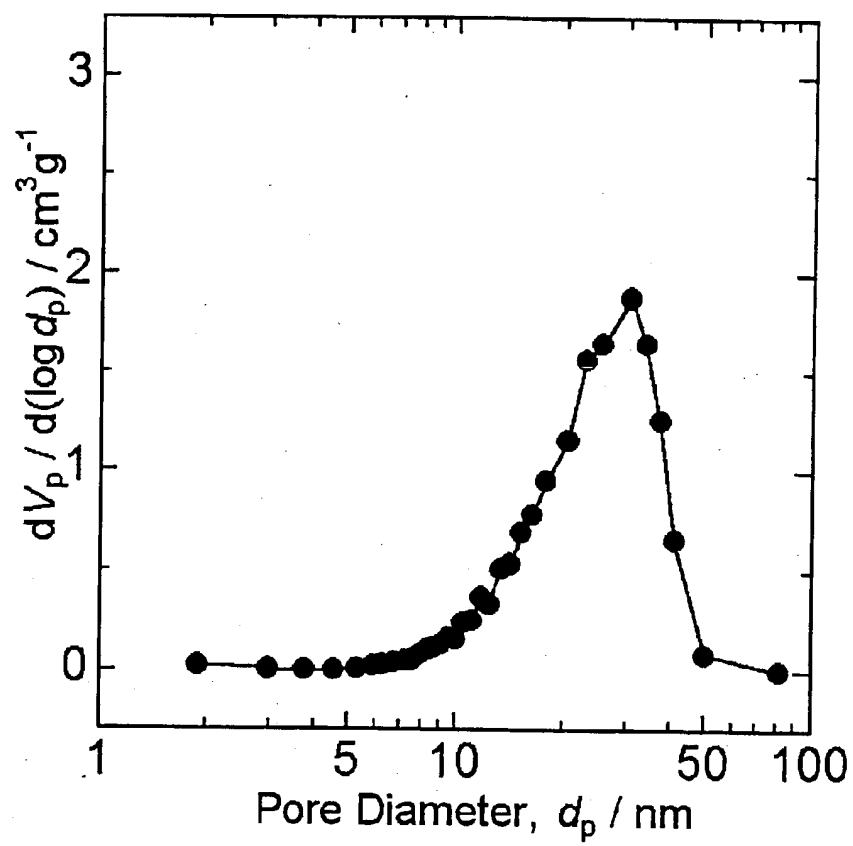
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Fig. 1



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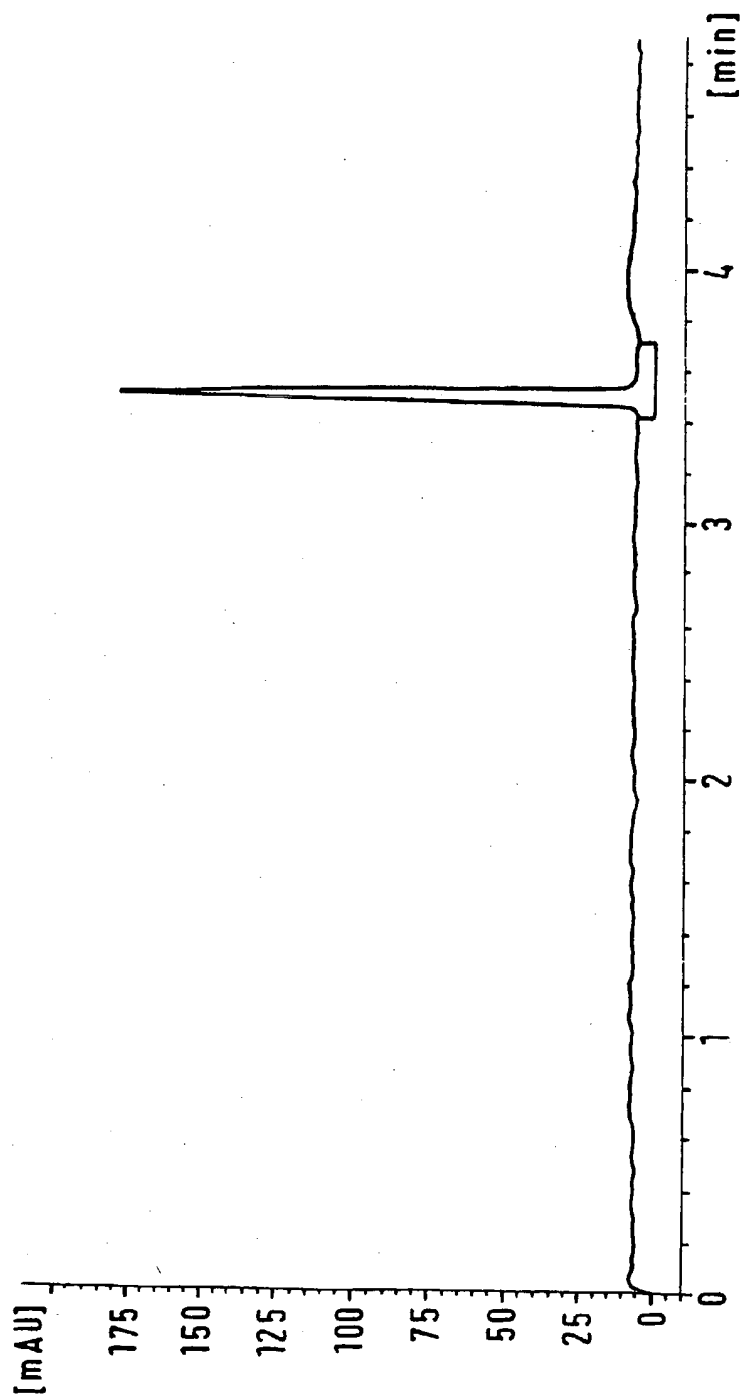


Fig. 2

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 98/08295

**A. CLASSIFICATION OF SUBJECT MATTER**  
 IPC 6 G01N30/56 G01N30/48

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 95 03256 A (MERCK PATENT GMBH ; SOGA NAOHIRO (JP); NAKANISHI KAZUKI (JP)) 2 February 1995 cited in the application	1
A	see page 23-24; claims 6-9 see page 16; example 5 ---	3
Y	US 5 647 979 A (LIAO JIA-LI ET AL) 15 July 1997	1
A	see page 4, line 21-45 ---	4-6
A	US 5 192 351 A (MATHUR AKSHAY ET AL) 9 March 1993 see column 8; claims 1,12,23 ---	1,2
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

7 April 1999

Date of mailing of the international search report

15/04/1999

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# INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 98/08295

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>JAYMES I ET AL: "New Aqueous Mullite Precursor Synthesis. Structural Study by Al and Si NMR Spectroscopy"</p> <p>JOURNAL OF THE EUROPEAN CERAMIC SOCIETY, vol. 16, no. 2, 1996, page 155-160</p> <p>XP004047243</p> <p>see page 155, column 2, paragraph 2 - page 156, column 2, paragraph 2</p>	1,2
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